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Molecular force fields for germanium compounds

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Molecular force fields of GeH_3F, GeH_3Cl, GeH_3Br GeH_3I were calculated using the kinematic methods suggested by Torkington, Herranz and Castano & Biles. It was found that the method suggested by Herranz & Castano gives satisfactory force fields for the lighter molecules GeH_3F and GeH_3Cl while the method suggested by Torkington leads to satisfactory force fields for the heavier molecules GeH_3Br and GeH_3I.

Introduction

The solution to the force constant problem is not unique and for an nth order secular equation, we obtain $n!$ solutions for the $1/2\ n(n+1)$ potential energy constants, corresponding to the $n!$ different ways af assignments. Solutions nearer to the correct one are obtained by using additional data like the isotopic vibrational frequencies, mean amplitudes, coriolis coupling coefficients and rotational distortion constants. Especially attempts by Duncan & Mills (1964a, 1964b), Aldous & Mills (1962, 1963) and Mirri (1967) using the coriolis coefficients and rotational distortion constants as additional data have yielded most satisfactory results. But for a majority of molecules all these constants are not available with great accuracy. Hence approximate solutions for the force fields are obtained using the simplified force fields like the Urey-Bradley force field (1931), the orbital valence force field (Heath & Linnet 1948) and the hybrid orbital force field (Mills 1963). Another way of obtaining a reasoneble force field for any molecule is the use of kinematic methods suggested by Torkington (1949), Biles (1966) and Herranz & Castano (1966a & 1966b). These methods use exclusively the geometry and the vibrational frequencies to fix the force field. The applicability of these kinematic methods to the XY_2 non-linear symmetric molecules was examined by Freeman (1968). In this paper the molecular force fields of the germyl halides were calculated using these kinematic methods and their relative merits discussed.

Potential energy constants

The characteristic features of these three kinematic methods are given below :

The method of 'progressive rigidity' suggested by Torkington (1949) consists in reducing the determinant product $|GF|$ in the secular determinantal equation $|GF-\lambda E| = 0$ to the product of its diagonal elements.

Here G is the Wilson's inverse symmetric (kinetic energy matrix, F is the force constant matrix, Λ a diagonal matrix with its element $\lambda_k = 4\pi^2\nu_k^2c^2$ where ν_k is the k^{th} vibrational wavenumber, and c is the velocity of light in cm sec^{-1} and E is the unit matrix. The conditions for the above mentioned reduction were given by Torkington (1949).

The symmetry coordinates used to construct G are arranged in the decreasing order of frequencies. The calculation of force constants becomes easy by defining two subsidiary matrices e and h obtained from the various minors of the G matrix. The general solution for the force constants is given by

$$F_{ij} = \sum_{k=i}^{n} (e_{ik}\, e_{jk}/e_{kk}\, h_{kk})\, \lambda_k \qquad (i>j) \qquad ...(1)$$

The matrix L which relates the set of symmetry coordinates S to the vibrational normal coordinates Q and given by $S = LQ$, is triangular in this method. Further the frequencies factor out in the decreasing order of magnitude and the molecule increases in rigidity as factorization proceeds.

In the method suggested by Biles (1966) the normal coordinate transformation matrix L is given as,

$$L = B\,\Gamma^{1/2} \qquad ...(2)$$

and the solution for the force field is given as

$$F = B\,\Gamma^{-1}\,\Lambda\,B^{*} \qquad ...(3)$$

where B is an orthogonal matrix which diagonalises G and Γ is a diagonal matrix having the eigenvalues of G as its elements, and Λ a diagonal matrix with the element $\lambda_k = 4\pi^2\nu_k^2c^2$. The asterisk denotes transposition of the matrix. Here the matrix product GF is symmetric.

In the method of 'characteristic set of valence coordinates' suggested by Herranz and Castano (1966a, 1966b) the normal coordinate transformation matrix L is symmetric. This method has been extensively used for fixing the force fields of some highly conjugated acetylenes (Ramaswamy & Srinivasan 1967, 1968). The present work deals with applicability of the above methods to a a series of germanium compounds.

The germyl halides discussed here belong to the C_{3v} point group and each has six fundamental vibrational frequencies of which three belong to the totally symmetric (a_1) species and three belong to doubly degenerate (e) species. The symmetry coordinates used are the same as those given by Meister & Cleveland (1946). The structural parameters used in the calculations are those given by Freeman *et al* (1963) The valence force constants calculated by the three methods are given in table 1,

TABLE 1 VALENCE FORCE CONSTANTS IN MDYNES/A° OF THE GERMYL HALIDES BY THE KINEMATIC METHODS

Valence force constants	GeH_3F Methods I	II	III	GeH_3Cl Method I	II	III	GeH_3Br Methods I	II	III	GeH_3I Methods I	II	III
f_D[1]	4.2488* (4.2130)[a]	4.2511	6.6055	2.5458 (2.5620)[a]	2.5504	10.2317	2.1290 (2.1180)[a]	2.1387	15.8820	1.7166 (1.7450)[a]	1.7285	18.4046
f_d[2]	2.6548 (2.6660)[a]	2.6563	0.2747	2.6509 (2.6670)[a]	2.6570	0.5845	2.6404 (2.6560)[a]	2.6418	0.1712	2.6272 (2.6360)[a]	2.6285	0.1558
f_α[3]	0.1597	0.1626	0.8559	0.1557	0.1602	0.7350	0.1549	0.1583	0.8578	0.1484	0.1518	0.5395
f_β[4]	0.1742	0.1759	0.4901	0.1300	0.1324	0.3531	0.1159	0.1177	0.3844	0.0990	0.1003	0.3414
$f_{\alpha\alpha}$	-0.0259	-0.0273	-0.1032	-0.0296	-0.0315	-0.1576	-0.0246	-0.0261	-0.0893	-0.0240	-0.0254	-0.0876
$f_{\beta\beta}$	-0.0397	-0.0405	0.0403	-0.0310	-0.0318	-0.0280	-0.0228	-0.0234	0.0345	-0.0191	-0.0197	0.0340
$f_{d\alpha}$	0.0028	0.0101	0.0062	0.0091	0.0330	0.1045	0.0026	0.0095	-0.0201	0.0025	0.0093	-0.0194
$f_{d\beta}$	0.0050	0.0180	-0.0084	0.0010	0.0112	-0.1092	0.0020	0.0131	0.0365	0.0017	0.0117	0.0051
f_{Dd}	0.0185	0.0554	0.0360	0.0105	0.0501	0.0546	0.0087	0.0548	0.0684	0.0070	0.0577	0.0760
f_{dd}	0.0032	0.0031	0.0169	0.0048	0.0052	0.2410	0.0072	0.0039	-0.0518	0.0055	0.0055	-0.0533

*This number of significant figures is retained to secure internal consistency in the calculations.

Method I-Method of progressive rigidity ; Method II-Method of characteristic set of coordinates ; Method III-Method suggested by Biles

f_D[1] = $f_{Ge\text{-}X}$ (X = F, Cl, Br, I); f_d[2] = $f_{Ge\text{-}H}$; f_α[3] = f_{HGeH} ; f_β[4] = f_{HGeX}.

Freeman *et al* (1963)

TABLE 2 MEAN AMPLITUDES OF THE GERMYL HALIDES AT $T = 298.16°K$

Mean amplitudes in A*	GeH_3F		GeH_3Cl		GeH_3Br		GeH_3I	
	Method I	Method II	Method I	Method II	Method I	Method II	Method I	Method II
Ge-X	0.0418* (0.039)[a]	0.0418	0.0464 (0.045)[a]	0.0465	0.0477 (0.048)[a]	0 0478	0.0518 (0.054)[a]	0.0519
Ge-H	0.0893	0.0893	0.0893	0.0894	0.0894	0 0894	0.0895	0.0895
H ..H	0.1532	0.1540	0.1530	0.1318	0.1543	0.1541	0.1553	0.1552
H...X	0.1241	0.1267	0.1350	0.1355	0.1390	0 1406	0.1448	0.1443

[a]Muller and Cyvin (1968).

*This number of significant figures is retained to secure internal consistency in the calculations.

TABLE 3 VALUES OF ROTATIONAL DISTORTION CONSTANTS D_j, D_{jk} AND D_k IN KC/SEC.

Rotational distortion constants in kc/sec.	GeH_3F		GeH_3Cl		GeH_3Br		GeH_3I	
	Method I	Method II	Method I	Method II	Method I	Method II	Method I	Method II
D_j	8.9500*	8 9323	1 9232	1.9124	0.6140	0.6123	0 2910	0 2903
D_{jk}	127.6549	130.3529	27.2071	27.1186	8.8245	8.8957	4 3968	4.1298
D_k	684.7540	671.6973	925 3866	866 1315	706.1169	697.4949	731.7817	723.0498

*This number of significant figures is retained to secure internal consistency in the calculations.

TABLE 4 CORIOLIS COUPLING CONSTANTS OF THE GERMYL HALIDES

Coriolis coupling constants	GeH_3F			GeH_3Cl			GeH_3Br			GeH_3I		
	Methods		Observed[a]	Methods		Observed[a]	Methods		Observed[a]	Methods		Observed[a]
	I	II		I	II		I	II		I	II	
ζ_4	0.0183*	-0.0019	-0.054	0.0179	-0.0319	-0.065	0.0185	-0.0013	-0.074	0.0185	-0.0011	-0.046
ζ_5	-0.2046	-0.1283	-0.110	-0.2366	-0.1192	-0.140	-0.1859	-0.1131	-0.101	-0.1854	-0.1123	-0.157
ζ_6	0.2483	0.1923	0.203	0.2447	0.1771	0.200	0.1826	0.1295	0.187	0.1771	0.1237	0.210
$\sum_i \zeta_{1i}$	0.0620	0.0621		0.0259	0.0260	-	0.0152	0.0152		0.0103	0.0103	
$I_A/2I_B$	0.0620	0.0620		0.0259	0.0259		0.0152	0.0152		0.0103	0.0103	

[a]Rhee and Wilson (1965).

*This number of significant figures is retained to secure internal consistency in the calculations.

Mean amplitudes

The symmetric mean square amplitude matrix Σ for both the species were evaluated using the relation given by Cyvin (1959),

$$\Sigma = L\triangle L^{*} \qquad \ldots(4)$$

where Δ is a diagonal matrix whose elements are given by

$$\triangle_{ii} = \frac{h}{8\pi^{2}c\nu_{i}} \coth\left(\frac{hc\nu_{i}}{2kT}\right) \qquad \ldots(5)$$

where h is the Planck's constant, K the Boltzmann's constant, T the absolute temperature, ν_i the i^{th} vibrational wavenumber.

The various bonded and non-bonded mean square amplitudes can be obtained as the linear combinations of the Σ matrix elements. The non-bonded mean square amplitudes were obtained by the method of Ramaswamy *et al* (1962). The mean square amplitudes were evaluated for all the four molecules using the L matrices obtained in the method of progressive rigidity and the method of characteristic set of coordinates. The computed mean amplitudes at $T = 298.16°K$ are presented in table 2.

Rotational distortion constants

For calculating the rotational distortion constants the rigid rotor harmonic oscillator approximation as suggested by Nielsen (1951) was assumed and the theory of Kivelson & Wilson (1952, 1953) was applied. For a molecule belonging to the C_{3v} point group, the rotational distortion constants D_j, D_{jk} and D_k alone exist and these can be expressed as linear combinations of certain elements denoted by τ. These constants can be evaluated from a knowledge of the principal components of the moment of inertia tensor, the vibrational wavenumbers and the 'l' matrix which relates the vibrational normal coordinates to the mass weighted Cartesian coordinates, The explicit relations are given in the paper by De Alti *et al* (1965).

The principal axis of the molecule is taken as the Z axis with one Ge-H bond lying in the XZ plane. The rotational distortion constants evaluated in the first two methods ate given in table 3.

Coriolis coupling constants

The coriolis coupling constants were evaluated using the relation given by Meal & Polo (1956)

$$\zeta^{\alpha} = |\, M^{\alpha}\, |^{*}$$

where $\alpha = (x,y,z)$ denotes the axis of rotation and M^{α} is a block diagonal supermatrix made up of n identical (3×3) submatrices one for each atom. The l matrices obtained in the first two methods were used

to calculate the ζ^{ϵ} values for the coupling between the components of the degenerate vibrations. They are presented in table 4.

The ζ sum rule for these symmetric top molecules is given by

$$\Sigma_i \zeta_i = I_A/2\, I_B$$

where I_A and I_B are the principal moments of inertia of the molecule.

Discussion

Barring the small interaction force constants the values of the stretching and bending force constants are very nearly the same in the first two methods. The values compare well with those given by Krishnamachari (1955), Pillai & Perumal (1964) and Freeman *et al* (1963). Going through the series some systematic trends are observed with the values of the force constants. The Ge-H stretching force constant in GeH_3F is about 2.7% greater than that in GeH_3I, The Ge-X stretching force constant markedly decreases with decreasing electronegativity of the substituted halogen. The value of the bending constant f_β decreases with decreasing electronegativity of the halogen while f_α is practically unaffected. These trends were also observed by Freeman *et al* (1963) The method of progressive rigidity gives smaller values for the interaction force constants. The values of the various force constants obtained by the method of Biles are in poor agreement with the reported values. Further they do not show any of the systematic trends noted above.

To see which of the first two methods gives a better approximation to the true force field in these molecules, other molecular constants like the mean amplitudes, rotational distortion constants and coriolis coupling constants were evaluated.

From table 2 it is clear that the values of the various mean amplitudes are the same in the two methods. The values obtained for the Ge-H and the H...H mean amplitudes are comparable to the corresponding values of 0.0895 A° and 0.1525 A° obtained by Cyvin (1968) for GeH_4. Also the calculated mean amplitudes for the Ge-X bonds can be compared to the values of Muller & Cyvin (1968) for the same bonds in GeX_4 molecules.

The values of the rotational distortion constants D_j, D_{jk} and D_k obtained in the two methods are also the same. Both D_j and D_{jk} markedly decrease with increasing mass of the substituted halogen. As seen from figures 1 and 2 the plots of log D_j and log D_k against log m_x where m_x is the mass of the substituted halogen give straight lines. Similar results were obtained by Rao & Rao (1968) for XY_3 type molecules belonging to the C_{3v} point group. This shows that the values of D_j and D_k obtained are reasonable. Since no experimentally observed values of these

constants are available no comparison of the calculated values can be made.

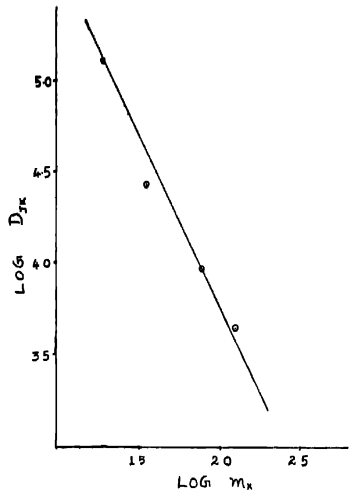

Figure 1

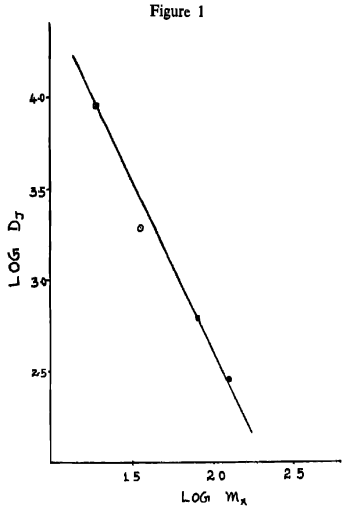

Figure 2

The coriolis coupling constants obtained in the two methods are different for all the four molecules, The ζ sum rule is perfectly verified in both the methods though agreement with the observed values is unsatisfactory. For GeH_3F and GeH_3Cl the value of ζ_5 and ζ_6 are closer to the observed values while they deviate more and more from the observed values as the mass of the substituted halogen increases, in the method suggested by Herranz & Castano. In the method suggested by Torkington the ζ values approach the observed values as the mass of the halogen increases.

From a study of these four molecules by the kinematic methods, it may be concluded that the method of 'Characteristic set of valence coordinates' suggested by Herranz & Castano gives a better approximation to the true force field, for the lighter molecules GeH_3F and GeH_3Cl while the method of 'progressive rigidity' suggested by Torkington seems to give a better approximation to the correct force field for the heavier molecules GeH_3Br and GeH_3I. The method suggested by Biles gives quite unsatisfactory force fields for these molecules. To fix exactly the proper force field for germanium compounds, further work along these lines with different germanium compounds is in progress.

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